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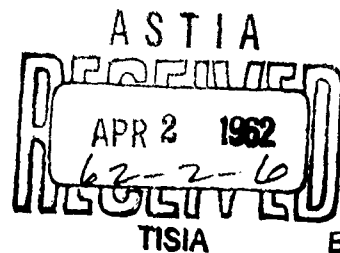
PROPERTIES AND STRUCTURE OF BORIDES
(SELECTED ARTICLES)

TRANSLATIONS FROM RUSSIAN BY
F. W. VAHLDIEK AND S. A. MERSOL

TECHNICAL DOCUMENTARY REPORT No. ASD-TR-61-514
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FOREWORD

This report is a compilation of four translations from the Russian literature. The translations were made by F.W. Vahldiek and S.A. Mersol of the Ceramics and Graphite Branch, Metals and Ceramics Laboratory, Directorate of Materials and Processes, of the Aeronautical Systems Division. This work was done under Project 7350, "Refractory Inorganic Nonmetallic Materials," Task 735001, "Ceramics and Cermet Materials Development."

ABSTRACT

Of the four translations included in this report, two concern SiB_6 : the X-ray determination of the SiB_6 structure, and some problems on the chemical compounds involving boron and silicon.

The third is a treatise on the heats of formation of the borides of some transition metals, with certain references to their carbides and nitrides. The fourth comprises a discussion of the pressing and sintering of TiB_2 and CrB_2 powders.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



W.G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Laboratory
Directorate of Materials and Processes

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CRYSTALLOGRAPHY

X-RAY DETERMINATION OF THE SiB_6 STRUCTURE

N.N. Juravlev

(Translation by F.W. Vahldiek)

The established crystallographic structure of the compound SiB_6 has a cubic lattice that is isomorphic to CaB_6 . The unit cell has the following dimension:

$$a = 4.142 \pm 0.002 \text{ KX - units}$$

Its pycnometrically determined density (1) with carbon tetrachloride, is

$$\sigma_p = 2.15 \text{ g/cm}^3$$

For the space group configuration o_H^I when Z is one, the X-ray density of SiB_6 is

$$\sigma_R = 2.18 \text{ g/cm}^3$$

The density of SiB_6 is less than the combined densities of Si and B, which may account for the stability of the compound.

The existence of the compound formation of Boron (B) with Silicon (Si) was first reported by Moissan in reference 2, in which he noted that by melting Si with B, two compounds, SiB_3 and SiB_6 , can be formed. Both are in the form of black crystals (3), possess an extreme hardness, and are good conductors of electricity. The density of SiB_3 is 2.52 g/cm^3 ; that of SiB_6 , 2.47 g/cm^3 .

Our investigations were concerned with the measurements of structure patterns of SiB_6 using X-ray techniques.

The specimens of SiB_6 , as received at the Moscow Institute of Gold and Nonferrous Metals, were prepared by G.V. Samsonov from the elements, Si and B, previously obtained by Mg-reduction of B_2O_3 and SiO_2 (quartz), respectively. The samples were dark in color.

The X-ray patterns were determined with an RKU camera having a diameter of 114.4 mm and Cu-K- α -radiation. First of all, our calculation showed the presence of a cubic phase in our specimens with a lattice parameter of $a = 4.14 \text{ KX units}$. This suggests the hypothesis that SiB_6 is present in the cubic hexaboride structure. A comparison of the CaB_6 and SiB_6 polycrystals indicated a similarity and proved the earlier theory of the isomorphism of these compounds.

The intensities and the d-spacings of the lines were measured from the X-ray patterns of the SiB_6 specimens (see table 1).

TABLE I
THE MEASUREMENTS AND CALCULATIONS OF THE SiB_6 X-RAY PATTERNS

hkl	$d_{\text{calc.}}$	$d_{\text{exper.}}$	$I_{\text{exper.}}$	$I_{\text{theor.}}$
1 0 0	4.1 4	—	—	0.1
1 1 0	2.9 3	2.9 3	very strong	4 6 3.
1 1 1	2.3 9	2.4 0	strong	1 9 9.
2 0 0	2.0 7	2.0 7	moderate	1 2 3.
2 1 0	1.8 5	1.8 5	strong	1 6 6.
2 1 1	1.6 9	1.6 9	very weak	1 4.5
2 2 0	1.4 6	1.4 6	very weak	1 5.8
3 0 0	1.3 8	1.3 8	strong	0.7
2 2 1	1.3 8			2 1 6. } 216.7
3 1 0	1.3 1	1.3 1	moderate	1 3 3.
3 1 1	1.2 5	1.2 5	weak	3 5.
2 2 2	1.1 9	—	—	0.3
3 2 0	1.1 5	1.1 5	very weak	1 2.
3 2 1	1.1 0 8	1.1 0 7	weak	3 2.3
4 0 0	1.0 3 6	1.0 3 5	weak	3 0.9
4 1 0	1.0 0 4	1.0 0 4	weak	3.5
3 2 2	1.0 0 4			5 7.3 } 60.8
4 1 1	0.9 7 7	0.9 7 6	moderate	2 2.5
3 3 0	0.9 7 7			5 5.6 } 78.1
3 3 1	0.9 5 1	—	—	1.4
4 2 0	0.9 2 7	0.9 2 7	weak	4 2.7
4 2 1	0.9 0 4	0.9 0 4	moderate	8 1.
3 3 2	0.8 8 4	0.8 8 4	weak	3 6.
4 2 2	0.8 4 5	0.8 4 5	very weak	3.2
5 0 0	0.8 2 8	—	—	1.2
4 3 0	0.8 2 8			1.6 } 2.8
5 1 0	0.8 1 2 3	0.8 1 2 4	strong	1 0 1.
4 3 1	0.8 1 2 3			1 4 9. } 249.
5 1 1	0.7 9 7 2	0.7 9 7 2	moderate	1 3 4.
3 3 3	0.7 9 7 2			0.2 } 134.2

The results of the exact measurements of the SiB_6 patterns gave us the value given in equation 1. The calculations of the interplanar spacings using this equation (see table 1) agree very well with those experimentally found, and the X-ray data of the SiB_6 phase indicated that its spacings also agreed with those of the already known hexaborides, CaB_6 , LaB_6 , etc. (4).

In a structure such as CaB_6 , the atoms possess the locations (a) and (f), in the lattice-spacing-group, O_H^I - Pm 3m (5) and,

Si 1(a) : 000;

B 6(f) : $\pm(x; \frac{1}{2}; \frac{1}{2})$.

In the Structural Peak Value,

$$F_{hkl} = f_{Si} + 2f_B \left[\cos 2\pi \left(hx + \frac{k+l}{2} \right) + \cos 2\pi \left(kx + \frac{h+l}{2} \right) + 2\pi \left(lx + \frac{h+k}{2} \right) \right],$$

the average value of the parameter x was 0.21. The intensities of the lines were calculated by the formula

$$I \sim L_p P F^2$$

where L_p is the Lorentz or polarization factor, and p is the frequency factor.

A comparison of the calculated and measured intensities showed good agreement.

The specimens studied were basically the SiB_6 phase and contained a small amount of impurities, probably SiO_2 and SiC , which showed a few weak additional lines in the pattern.

The difference in the values for the SiB_6 density, ours and that recorded in the literature, can probably be explained by the differing amounts of impurities in the specimens. The hexaboride has a simple cubic lattice structure, in which all boron atoms form a three dimensional shell, and in between are the metal atoms which in the case of SiB_6 are the Si atoms. The B atoms form into an octahedron, each surrounded by five other B-atoms in the distance of 1.72 KX units. Four of the five atoms gather in the same octahedron, the fifth goes to a neighboring unit. Each B atom is surrounded by four metal atoms; likewise, four metal atoms and one B atom form a tetragonal pyramid.

The metal atom may form into a number of possible combinations; for instance, six metal atoms can be surrounded by 24 B atoms. A comparison of the distance between metal atoms and the distance between B atoms shows that this is considerably larger than the sum of the atomic radii. This shows that the formation of the B atoms has a stable structure, and the metal atoms are located in the empty spaces (6).

In the SiB_6 compound, the Si-atomic radius is considerably smaller than that of all known metals which form the hexaborides, and the distance from Si to B differs very much from the sum of the atomic radii of both together, for which:

$$\begin{aligned} Si + B &= 3.05 \text{ KX - units;} \\ R_{Si_{12}} &= R_{B_{12}} = 1.34 + 0.91 \\ &= 2.25 \text{ KX - units} \end{aligned}$$

Perhaps these characteristics of the SiB_6 structure help to explain the difficulty in making the compound SiB_6 (7).

The following people contributed to the results discussed in this paper: Prof. G.S. Gdanov, honorable director, and M.M. Umansky, instructor, for solid-state physics; A.A. Stepanova assisted by making many of the X-ray patterns of hexaboride; and G.V. Samsonov, instructor of metallurgy for rare metals, assisted in making the specimens.

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CHEMISTRY

ON THE PROBLEMS OF THE CHEMICAL COMPOUNDS OF BORON
WITH SILICON

Professor G.V. Samsonov and V.P. Latisheva

(Presented to the Academy of the USSR by
A.N. Frumkin on 10 June 1955)

(Translation by F.W. Vahldiek)

Compounds of boron with silicon, B_3Si and B_6Si , prepared from the elements, were mentioned by Moissan and Stock in reference 1. They also reported that these compounds are conductors of electricity, possess extreme hardness and a high chemical stability. Later attempts were made to produce these borides (2 and 3); however, no satisfactory results were obtained.

B.T. Baltaks (4) reported the interesting influence of the addition of boron on the resistivity of silicon. About 1 percent by weight of B added to Si increases the resistivity and the temperature coefficient; but this resistivity suddenly decreases and metallic conductivity appears.

We investigated and synthesized the compounds Moissan made from elementary B and Si. The synthesis may be accomplished by sintering a mixture of powdered B and Si from elements of high purity and by hot-pressing, which has the advantage of obtaining usable nonporous samples within the range of 1600° to 1800°C. The reaction was performed in an Argon-atmosphere. The resultant compound, corresponding to B_3Si , decomposed to B_6Si when fired, indicating a low temperature stability of the compound B_3Si when compared with B_6Si . The specific gravity of the B_3Si powder was determined micro-pycnometrically (5), and yielded values from 2.41 to 2.49 g/cm³. Using a load of 30 g yielded a micro-hardness range of 5352-167 Kg/mm². (Compare this with the micro-hardness value 3340-242 Kg/mm² for Boron and 1808-76 Kg/mm² for Silicon.)

In our X-ray study, using the powder method with Cu-radiation and an exposure time of from 8 to 10 hours, we obtained proof of the presence of B_3Si in the tetragonal lattice structure with $Z = 1$, and the axes $a = 2.829 \pm 0.007 \text{ \AA}$; $c = 4.765 \pm 0.013 \text{ \AA}$; and $c/a = 1.68$.

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PHYSICAL CHEMISTRY

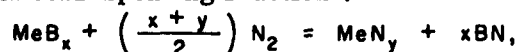
HEATS OF FORMATION OF BORIDES OF SOME TRANSITION METALS

Professor G.V. Samsonov

(Translation by S.A. Mersol)

In view of the increasing requirements for borides of transition metals, the determination of the heats of formation of corresponding boride phases becomes particularly important. Partial facts on this subject have been published recently, in which during an analysis of the tensimetric curve of the formation of TiB_2 , the heat of formation of TiB_3 was determined by the vacuum-thermal method, and was found to be equal to ~ 70.04 kcal/mole (1).

In Brewer's and Haraldsen's work (2) the thermodynamic stability of borides of refractory metals, Ti, Zr, Nb, Ta, Cr, Mo, and W (also Ce and Th), were discussed. To determine the approximate values of the heats of formation of the borides, they used the data on the stability of borides to nitrogen and carbon; these data were obtained by X-ray analysis of the products of corresponding reactions:



In such an analysis if no solubility of the initial components or of the reaction products takes place, or if no other new compounds are formed, it is possible to determine the approximate values of heats of formation of borides, as well as those of boron nitrides and carbides from values established by previous investigations (see data in table 1).

TABLE 1 (2)
THE HEATS OF FORMATION OF BORIDES OF TRANSITION METALS

BORIDE	ΔQ KCAL/MOLE	BORIDE	ΔQ KCAL/MOLE	BORIDE	ΔQ KCAL/MOLE	BORIDE	ΔQ KCAL/MOLE
TiB_2	~ 72	NbB_2	> 36	MoB	16.3	W_2B_5	25 - 45
Ti_2B_3	> 105	TaB_2	> 52	MoB_2	23.0	CeB_4	< 84
ZrB	> 39	CrB_2	> 30	Mo_2B_3	50.0	ThB_4	> 52
ZrB_2	> 78	Mo_2B	25.5	W_2B	20 - 28	ThB_6	> 66
ZrB_{12}	> 120	Mo_3B_2	42.0	WB	12 - 22	—	—

Note that the general thermodynamic stability of the compounds which transition metals form with metalloids like boron, carbon, and nitrogen is, in large degree, determined not only by the reaction kinetics of the compounds being formed, but also by the degree of matching of the electronic configuration and the atom of the metal (or non-metal) whereby energetically the least stable is more directly affected. Matching the electronic configuration to the atom of the metal or nonmetal must be accompanied by the formation of energetically more stable states, in which either the d-orbitals of metal

atoms are "filled up" or there is a release of energy close to the ionization energy of the nonmetal atom (3). It follows, then that the smallest heats of formation values of the molecules are found in carbides (ionization potential of carbon $I_c = 11.22$ eV), and much greater values in nitrides ($I_n = 14.47$ eV), borides ($I_b = 8.4$ eV) and silicides ($I_{si} = 7.39$ eV)*. As to the filling up of d-orbitals of transition metal atoms having various electronic defects, it seems proper to assume that within each transition period the heats of formation must decrease with a corresponding decrease in electronic defect of the metal.

In Table 2 values are listed for the heats of formation of borides, carbides, and nitrides of transition metals per mole of the phase and per g-atom of the nonmetal.

TABLE 2
HEATS OF FORMATION OF BORIDES, CARBIDES, AND NITRIDES

METAL	HEAT OF FORMATION IN KCAL								
	BORIDE			CARBIDE			NITRIDE		
	PHASE	PER MOLE OF PHASE	PER G ATOM OF B	PHASE	PER MOLE OF PHASE	PER G ATOM OF C	PHASE	PER MOLE OF PHASE	PER G ATOM OF N
Ti	TiB ₂	72	36	TiC	57.25	57.25	TiN	80.3	80.3
V	VB ₂	—	—	VC	28.0	28.0	VN	60.0	60.0
Cr	CrB ₂	>30	>15	Cr ₃ C ₂	21.01	10.50	CrN	29.5	29.5
Zr	ZrB ₂	>78	>39	ZrC	44.1	44.1	ZrN	82.2	82.2
Nb	NbB ₂	>36	>18	NbC	19.0	19.0	NbN	59.0	59.0
Mo	MoB ₂	23	11.5	MoC	-4.2	-4.2	MoN	17.0	17.0
Hf	HfB ₂	—	—	HfC	—	—	HfN	—	—
Ta	TaB ₂	>52	>26	TaC	38.5	38.5	TaN	58	58
W	W ₂ B ₅	25 — 45	5 — 9	WC	-8.4	-8.4	WN	17	17

Additionally, the determination of the heats of formation is largely dependent on the nonmetal's ionization potential. By increasing the number of metalloid atoms per metal atom (as in boride phases) the heat of formation of the bond Me-B (Q per 1 boron atom) decreases as a result of the transition its electrons make to form covalent bonds B-B. More specifically (from the data in table 1), it follows that

$1/2 \text{ TiB}_2 \sim 36$	$\text{Mo}_2\text{B} \quad 25.5$
$1/2 \text{ Ti}_2\text{B}_5 > 21$	$1/2 \text{ Mo}_3\text{B}_2 \quad 21$
$\text{ZrB} > 39$	$\text{MoB} \quad 16.3$
$1/2 \text{ ZrB}_2 > 39$	$1/2 \text{ MoB}_2 \quad 11.5$
$1/2 \text{ ZrB}_{12} > 10$	$1/5 \text{ Mo}_2\text{B}_5 \quad 10.0$

There is an increase in the tendency toward the formation of individual structural elements from boron atoms in the borides of transition metals (4). In figure 1 the data of table 2 on the heats of formation of boride, carbide, and nitride phases per one g-atom of the metalloid are shown graphically. For nitride and carbide phases within each transition period the Q values plot as straight lines, which enables us to extrapolate the heats

* Without the calculation of the metalloid-metalloid bonds.

of formation of HfC and HfN (not heretofore mentioned in the literature). These values are ~ 81 and ~ 97 kcal/mole, respectively. In diborides the boron atoms form horizontal lattices, perpendicular to the axis z , with layers of boron and metal atoms alternating in the arrangement ANAN. Changes in the positioning of the atoms in the horizontal lattices in Mo_2B_5 and W_2B_5 result in a relatively abrupt increase in the heat of formation for the Me-B bond, which, in turn, upsets the straight-lined dependency. However, this upset is taking place also in the boride phases CrB_2 and MoB_2 , with structures like AlB_2 , as well as in the rest of the borides. This reaction is apparently associated with those properties of the chromium and molybdenum atomic structure to which L. Pauling (5) first directed attention, i.e., that chromium contains only 5.78 bond electrons and is characteristically close to the elements of the iron triad and to the platinoids. This situation causes a relatively slow weakening of the electronic configuration to take place and in the observed phenomenon of unusually high values for the heats of formation of boron bonds. As the graphs in figure 1 indicate, it is impossible to determine the heats of formation of borides and other phases of iron, cobalt, and nickel by means of simple extrapolation.

An analogous picture (figure 2) is also obtained by the expression of heats of formation depending on the oxidizability (3) of transition metal atoms using

$$\epsilon = \frac{1}{M n} ,$$

where n equals the number of electrons and N equals the principal quantum number of vacant d-orbital spaces. This shows the presence of a deep bond between the heats of formation and the state of the electronic configuration of carbides, nitrides, and borides.

By the method described in reference 1 we also determined the heats of formation of diborides of zirconium (63.1 kcal/mole) and chromium (19.0 kcal/mole)*. We calculated the ΔQ of borides according to Kubashevskiy (6) by making use of the change in the molar volume at the formation of the compounds from the elements. Besides this, the data on the heats of formation of borides were obtained by extrapolation using the rectilinearity of the change ΔQ with the change of the metal atomic number in analogous phases, starting with the tensimetrical value $\Delta Q_{\text{TiB}_2} = 70.04$ kcal/mole. All these data are listed in table 3.

TABLE 3
THE COMPARISON OF THE HEATS OF FORMATION
OF BORIDES ACCORDING TO VARIOUS DATA

BORIDE	HEAT OF FORMATION IN KCAL			
	BY DATA FROM (2)	BY DATA FROM TENSIMETRIC EXPERIMENTS	CALCULATION ACCORDING TO (6)	EXTRAPOLATION BY GRAPHS OF FIGS. 1 AND 2
TiB_2	~ 72	70.04	73	—
ZrB_2	> 78	63.1	65	60
VB_2	—	—	62	24
NbB_2	> 36	—	59	33.5
TaB_2	> 52	—	63	45.0
CrB_2	> 30	19.0	47	—
MoB_2	22.5	—	60	—
W_2B_5	25 — 45	—	49	—

* The data on the chromium boride were obtained jointly with R.B. Kotelnikov.

It is possible to calculate from the established data the approximate values for the heats of formation of diborides of Ti, Zr, Nb, Ta, and Cr whereby the calculation by extrapolation apparently gives better results than those obtained by Kubashevskiy's empirical formula.

SUMMARY

A comparison was made between the numerical values of the heats of formation of borides of several transition metals of groups IV, V, and VI in the periodic system. These values were obtained through calculations and were determined as a result of tensimétrical experiments and the study of the products of the interaction of borides with nitrogen and carbon. It was shown that the heats of formation of compounds similar to metals (borides, carbides, and nitrides of transition metals) are determined by the distribution of the electron configuration in their crystal lattices.

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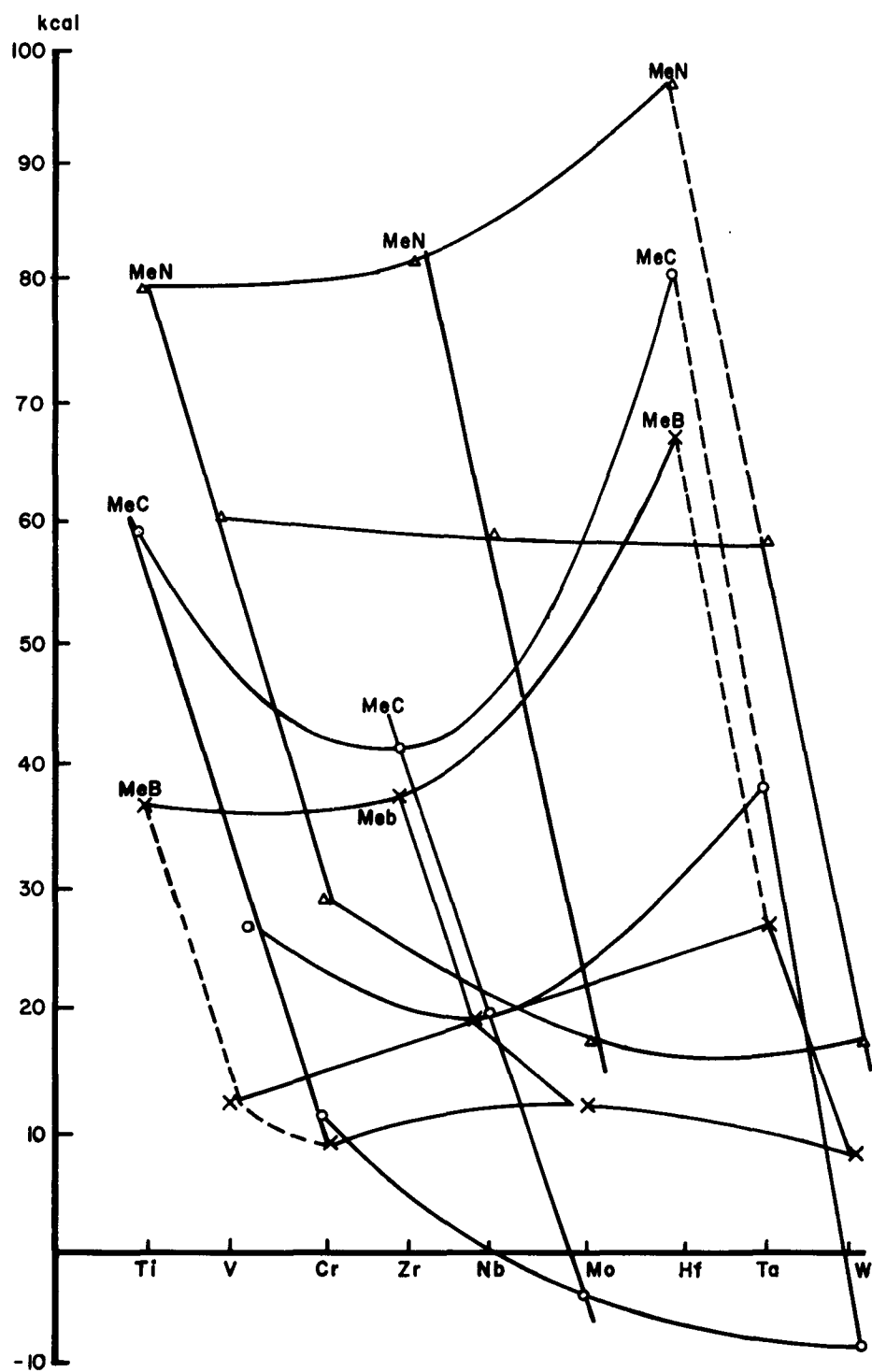


Figure 1. The heats of formation of carbides, borides, and nitrides (per 1 g-atom of metalloids).

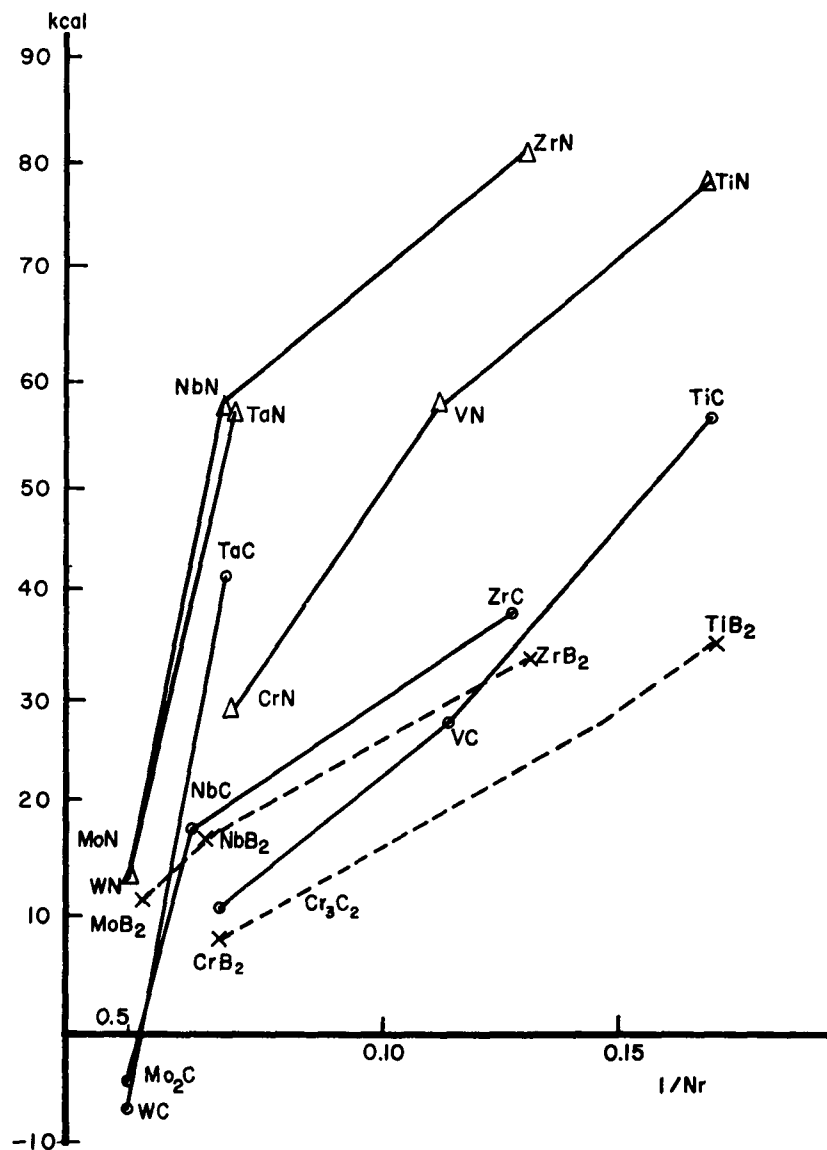


Figure 2. The relationships between the heats of formation of carbides, borides, and nitrides, and the value $1/Nr$ for transition metals.

CERAMIC ENGINEERING

PRESSING AND SINTERING OF BORIDE POWDERS

B.N. Babich
K. I. Portnoy
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(Translation by S.A. Mersol)

INTRODUCTION

Greater utilization of products made of borides or of alloys having a boride base (1, 2) made it necessary to establish a program for studying the powder metallurgy of these compounds.

Our investigation started with a study of reference 3. It was shown there that powders of hard materials sinter by means of the gradual breakdown of the uneven portions of the grains which are in contact with each other during their mutual migration. A determination of the degree of brittleness of powders of hard compounds is proposed, and the connection between the brittleness and the stability of the bond in the crystal lattice of the compound is indicated (3).

Chiotti (4) used the method of the separate pressing and sintering of specimens made of carbides of refractory metals. To facilitate sintering, he made use of the formation of the liquid phase with the addition of iron (up to 8 percent) or iron salt (up to 2.5 percent); the final content of the impurity in the specimen did not exceed 0.5 percent.

In the sintering process of refractory compounds (carbides and oxides), the main reason for the shrinkage of sufficiently pure compounds during sintering is that during heating the particles attain a plasticity, which is sufficient for the grains to be pulled into pores under the influence of the forces of surface tension and in the direction of the center of gravity of the pellet (5).

This process, often accompanied by recrystallization, starts above a homologous temperature of 0.8 ($T_{\text{sintering}} : T_{\text{melting}}$). The porosity of the sintered object can be reduced to values of less than 10 percent. This theory agrees with G.A. Myerson's theory of sintering, developed for plastic metals (6).

We investigated the conditions of pressing and sintering of TiB_2 and CrB_2 powders as well as those of the titanium and chromium boride alloy (the ratio of molar concentrations of $\text{TiB}_2 : \text{CrB}_2 = 4 : 1$).

The initial TiB_2 and CrB_2 powders were prepared in vacuum. Then $(\text{Ti}, \text{Cr})\text{B}_2$ was prepared from the specific mixture of these borides at 1700°C for one hour in vacuum.

The average particle diameter of the pellets of all three powders measured from 2 to 3 microns. Their loose-packed weights and their close-packed weights are shown in table 1.

TABLE I
THE LOOSE - PACKED WEIGHT AND THE CLOSE - PACKED WEIGHT OF BORIDE POWDERS

BORIDE	LOOSE - PACKED WEIGHT	CLOSE - PACKED WEIGHT	$\frac{\gamma_{\text{CLOSE - PACKED}}}{\gamma_{\text{LOOSE - PACKED}}}$
TiB ₂	0.80	1.24	1.55
CrB ₂	1.05	1.64	1.57
(Ti,Cr)B ₂	0.97	1.53	1.58

PRESSING

The specimens were pressed in a steel cylindrical die on a hydraulic press at pressures of from 0.5 to 8 tons/cm². For all tests the specimens had a diameter of 15 mm and were from 6 to 10 mm high. A study of the pressing procedure (9) involved a determination of the influence of the maintained pressure on the density of the pressed pellets by measuring their elastic properties and by studying the influence that interstitial wear or rubbing had had on their density.

The pellets proved to be of low strength, and the tremendous wear of the dies used for dry pressing made it necessary to mix plasticizers with the powders. The following plasticizers were used: a solution of synthetic rubber in gasoline (400 ml of 4 to 5 percent solution to 1 kg of the powder), a solution of Na₂SiO₃ in alcohol (the content of Si in the mixture was 1 percent), and a solution of FeCl₃ in alcohol (the content of Fe in powder was 1 percent).

The density of the pressed specimens was determined by the pressing rate and the applied pressure. To test the pellets' elasticity, the distance from the base of the die to the upper end of the die (the plunger) was measured and considered its indicator; the correction for the elastic compression of the plunger under load was entered, and the height of the pellet after pressing was measured.

None of the above listed plasticizers markedly improved the compressibility; however, the strength of the pellets was greatest when the FeCl₃ solution was used, and was therefore used in subsequent experiments.

Figure 1 shows the results of pressing at various compacting pressures. As the data indicates, TiB₂ performed better than CrB₂. Lamination phenomena during pressing started in the pressure range above 3 to 4 tons/cm².

Figure 2 shows a compacting pressure diagram in logarithmic coordinates, $\log p_{sp} - \log \beta$, where β is the relative volume $\beta = \frac{\gamma_{\text{compact}}}{\gamma_{\text{pellet}}}$, from which it follows that the pressing process is well expressed by the straight lines:

$$\text{For TiB}_2, \log p_{sp} = -11.07 \log \beta + 3.02$$

$$\text{For CrB}_2, \log p_{sp} = -10.48 \log \beta + 3.25$$

$$\text{For (Ti,Cr)B}_2, \log p_{sp} = -11.29 \log \beta + 3.24$$

where p_{sp} is specific pressure.

The continuance of pressure from 15 to 60 seconds does not have any effect on the density of the pressed pellet or briquette.

The continued process of rubbing pre-pressed specimens over the sieve 0105H with subsequent pressing at the same pressure allows the density of the pressed samples to increase for about 5 percent, whereby the greatest effect is produced by the first rubbing.

Figure 3 shows the results of the elasticity determination. When the results are compared with those obtained by an analogous investigation performed on metallic powders (9), it is notable that the length of time for which the powders were subjected to the pressure had no effect on the density of the boride pellets. This proves the practically complete nonplasticity of the pellets and the conservation of a highly strained state after pressing.

The relative elasticity of borides after pressing is in complete agreement with the high hardness of borides, since by comparison (9) the very hard tungsten carbide has a tremendous elastic effect after pressing. This also corresponds to the data of work (10). The elastic effect on the borides increases with the increase of the pressure to from 1 to 2 tons/cm². The decrease in magnitude of the elastic effect, which occurs at very high pressures, is due to the breakdown and hardening of the pressed pellets and to the distribution of fine-grained broken-off particles in-between larger unbroken particles. At still higher pressures, the elastic effect again increases; this is accompanied simultaneously by lamination phenomena. Technically, it is possible to consider the compacting pressure of 3 tons/cm² as the most favorable one, and at this pressure it is expedient to employ multiple pressing techniques.

In our studies of borides the most pronounced elastic effect in the powder borides occurred in the hardest boride, namely, TiB₂ (3370 kg/cm²), and in case of the solid-solution boride, in (Ti, Cr)B₂ (about 3800 kg/mm²). The elastic effect on CrB₂, whose hardness is 1800 kg/mm², is considerably smaller.

SINTERING

The conditions of sintering were studied by first compacting the pellets under the chosen pressure of 3 tons/cm². The sintering was performed at a pressure of 0.1 mm Hg in a vacuum tube furnace having a graphite heater (11). To determine the optimum sintering temperature, the specimens were sintered within the 1700° to 2400°C range for one hour.

The specific gravities of the sintered specimens were determined by hydrostatic suspension, and the linear shrinkage by the resultant heights (table 2).

TABLE 2
RESULTS OF THE SINTERING OF BORIDES

BORIDE	CHARACTERISTICS OF THE MATERIAL	SINTERING TEMPERATURE IN °C							
		1700	1800	1900	2000	2100	2200	2300	2400
TiB ₂	DENSITY IN G/CM ³	—	3.31	3.49	3.49	3.47	3.63	3.81	4.04
	RESIDUAL POROSITY IN %	—	25.5	21.6	21.6	22	18.4	14.3	9.1
CrB ₂	DENSITY IN G/CM ³	3.52	3.83	4.01	4.25	4.30	M E L T E D		
	RESIDUAL POROSITY IN %	37.1	31.6	28.4	24	23.2			
(Ti,Cr)B ₂	DENSITY IN G/CM ³	—	3.70	3.86	—	3.84	3.91	4.20	4.45
	IN %	—	22.4	19	—	19.4	18	11.9	6.7

From the table we see that the sintering process occurs in two stages: (1) minor density increase at the temperature up to 2100° or 2200°C, and (2) intensive density increase above 2100° or 2200°C. It is evident that in the second stage the plasticity of borides becomes sufficiently great to have surface tension overcome the strength of the particles. In all cases the reduced temperature at the beginning results in an increased density of from 0.7 to 0.8. The optimum sintering time was determined by holding TiB₂ and the solid solution (Ti, Cr)B₂ at 2300°C; CrB₂ was held at 2000°C (table 3).

TABLE 3
THE CORRELATION BETWEEN THE BORIDE SPECIMENS
DENSITY AND THE SINTERING TIME

BORIDE	SINTERING TEMPERATURE IN °C	SINTERING TIME IN MIN.	DENSITY IN G/CM ³	RESIDUAL POROSITY IN %
TiB ₂	2300	30	3.72	16.4
		60	3.80	14.3
		120	3.81	14.2
		240	3.79	14.4
CrB ₂	2000	30	4.18	25.6
		60	4.25	24
		120	4.26	23.9
		240	4.26	23.9
(Ti,Cr)B ₂	2300	30	4.16	12.5
		60	4.20	11.9
		120	4.20	11.9
		240	4.22	11.6

At the sintering temperatures selected the equilibrium between the stability of the particles and the surface tension is established rather rapidly; the higher the sintering temperature, the faster it progresses. In all cases, but especially in the case of TiB_2 and $(\text{Ti}, \text{Cr})\text{B}_2$, the low porosity of the specimens resulted from sufficiently high temperatures. As the temperature was increased, the attainment of a porosity approaching zero did not present special difficulties. CrB_2 is an exception, for its lowest porosity amounts to 23 percent and at the increased temperature (higher than 2100°C), melting begins. (The melting temperature of CrB_2 , 1900°C , as often cited in literature, is incorrect. According to the data in references 12 and 13, it is at 2200°C . It seems that this discrepancy is due to the dissociation of CrB_2 in the range of temperatures close to its melting point.)

CONCLUSIONS

The densification process of TiB_2 , CrB_2 , and $(\text{Ti}, \text{Cr})\text{B}_2$ powders is described by the logarithmic correlation between the relative volume and the compacting pressure. The resultant elastic effects of the materials studied is rather high. The dependence of the elastic effect on pressure is connected with the high brittleness and nonplasticity of the borides.

The process for achieving increased densities in boride pellets by sintering consists of drawing particles into the pore spaces upon attainment of that temperature at which the forces of surface tension prevail over the strength of the particles which become plastic.

The possibility of using separate cold pressing and sintering instead of the complex and uneconomical method of hot pressing was demonstrated.

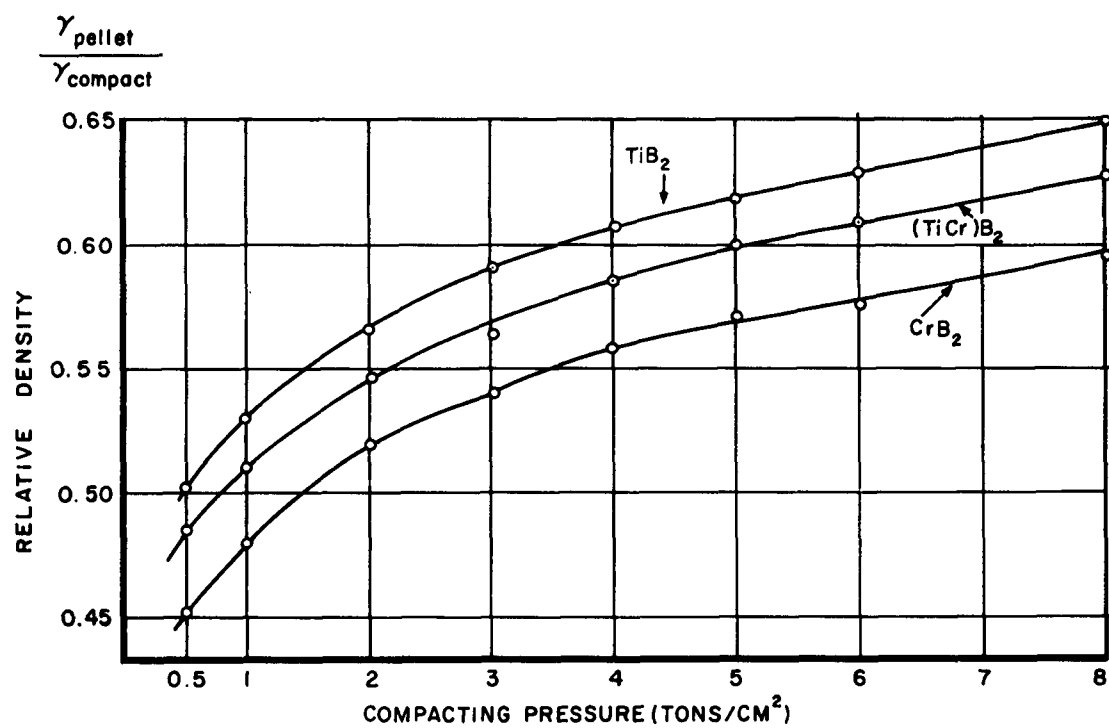


Figure 1. Correlation Between Relative Density and Compacting Pressure

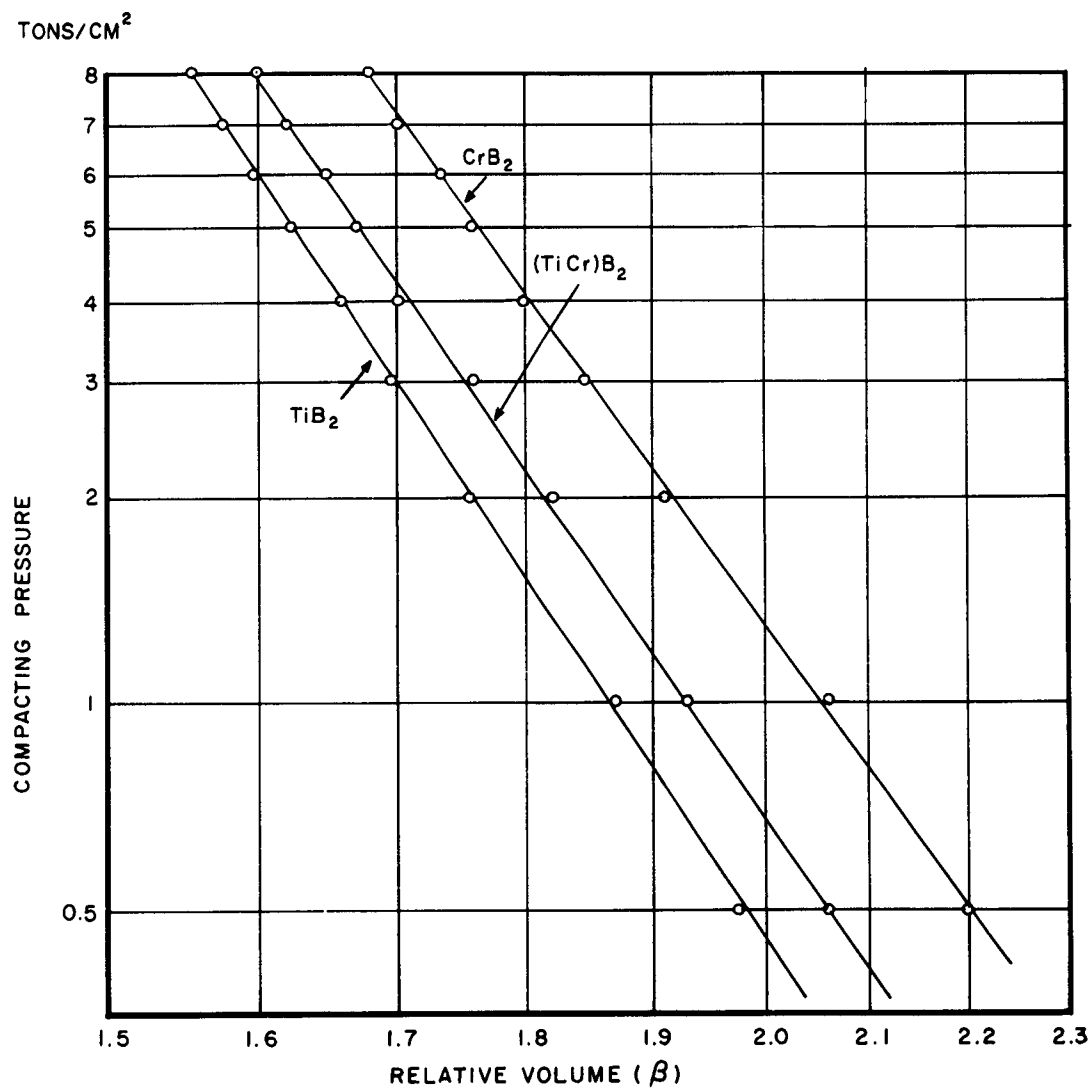


Figure 2. Correlation Between the Relative Volume and the Compacting Pressure

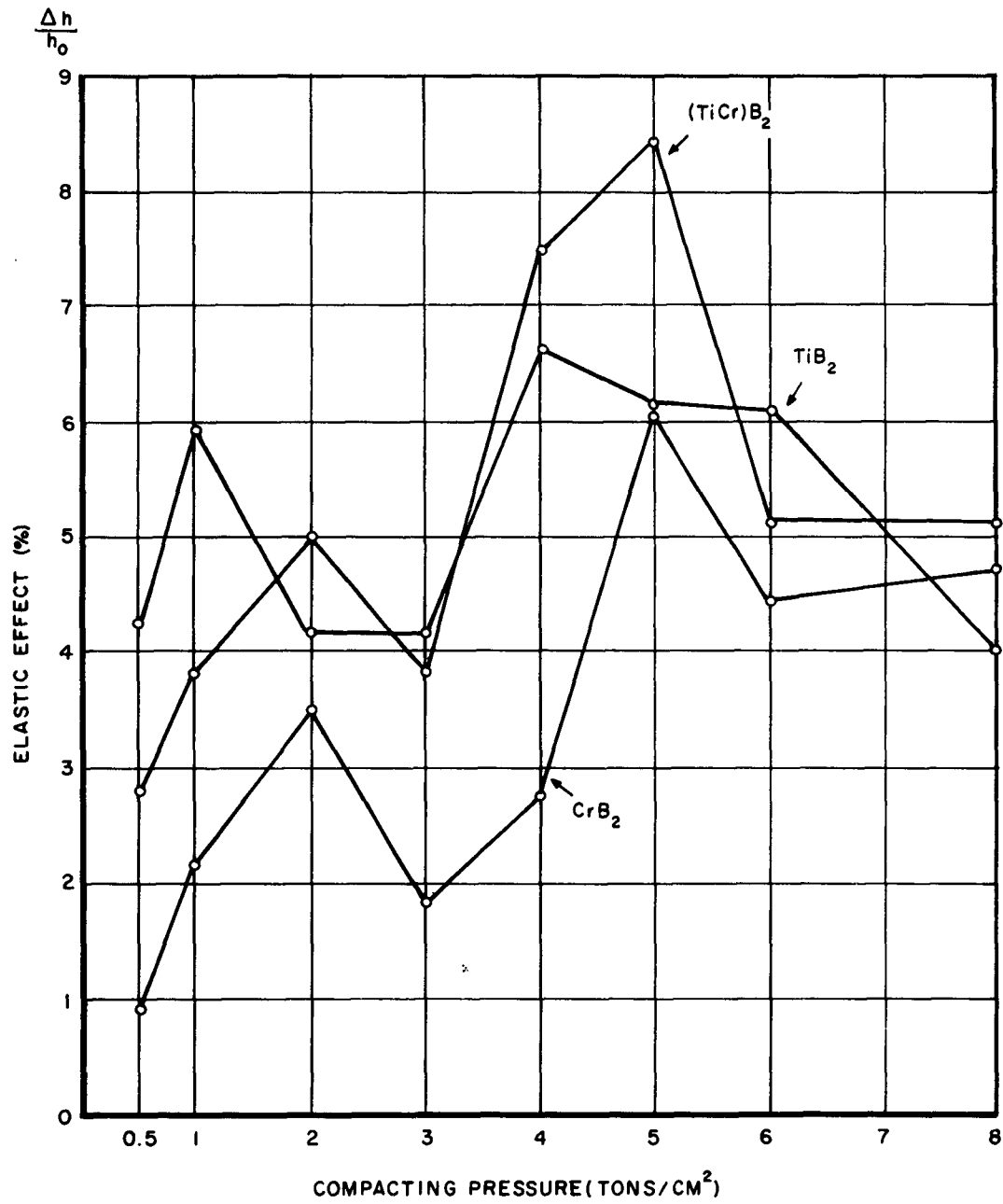


Figure 3. Correlation Between Elastic After-effect and Compacting Pressure

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<p>Metals and Ceramics Laboratory, Directorate of Materials and Processes, Aeronautical Systems Division, Wright- Patterson Air Force Base, Ohio. PROPERTIES AND STRUCTURE OF BORIDES, Selected Articles, by F.W. Vahldiek and S.A. Mersol. January 1962. 23 p. incl illus (Proj. 7350; Task 735001) (ASD TR 61-514) Unclassified report.</p>	<p>UNCLASSIFIED</p>	<p>Metals and Ceramics Laboratory, Directorate of Materials and Processes, Aeronautical Systems Division, Wright- Patterson Air Force Base, Ohio. PROPERTIES AND STRUCTURE OF BORIDES, Selected Articles, by F.W. Vahldiek and S.A. Mersol. January 1962. 23 p. incl illus (Proj. 7350; Task 735001) (ASD TR 61-514) Unclassified report.</p>	<p>UNCLASSIFIED</p>
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